

MM 10: Battery Materials

Theory

Time: Monday 15:45–17:00

Location: H 0106

MM 10.1 Mon 15:45 H 0106

Exploring structure and conductivity of the lithium super-ionic conductors $\text{Li}_{10}\text{GeP}_2\text{O/S}_{12}$: a first-principles molecular dynamics study — •GIULIANA MATERZANINI¹, LEONID KAHLE¹, ARIS MARCOLONGO^{1,2}, and NICOLA MARZARI¹ — ¹Theory and Simulations of Materials (THEOS), EPFL, Lausanne, Switzerland — ²IBM RSM Zurich Research Laboratory, Zurich, Switzerland

With the aim of finding superior lithium-ion conducting solids to replace the highly reactive liquid electrolytes typically used in rechargeable batteries, Lisicon-type materials (with orthorhombic or monoclinic cells) have been extensively studied in the last decades. Recently, following the experimental discovery of a highly conductive tetragonal phase for the thio-Lisicon $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, a theoretical study predicted the same phase for $\text{Li}_{10}\text{GeP}_2\text{O}_{12}$ to be poorly conducting. In this work we address the conductivity of $\text{Li}_{10}\text{GeP}_2\text{O}_{12}$ and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ through Car-Parrinello molecular dynamics, tuned to achieve an optimal thermalization between the heavy species and the light Li ions. The simulations feature extended thermostatted thermalization followed by microcanonical evolution. Last, NPT variable cell dynamics simulations within the Parrinello-Rahman scheme were also performed to complete exploration of the configurational space, since in these superionic materials there is not a corresponding unique ground state structure. A thorough analysis of the conducting performance for the oxide and the sulphide is presented.

MM 10.2 Mon 16:00 H 0106

Superionic diffusion through frustrated energy landscape — •DAVIDE DI STEFANO¹, ANNA MIGLIO¹, KOEN ROBEYNS¹, YAROSLAV FILINCHUK¹, MARINE LECHARTIER², ANATOLIY SENYSHYN³, HIROYUKI ISHIDA⁴, STEFAN SPANNENBERGER⁵, DENISE PRUTSCH⁶, DANIEL RETTENWANDER⁶, MARTIN WILKENING⁶, BERNHARD ROLING⁵, YUKI KATOH², and GEOFFROY HAUTIER¹ — ¹Université catholique de Louvain, Louvain-la-Neuve, Belgium — ²Toyota Motor Europe NV/SA, Zaventem, Belgium. — ³Technische Universität München, Garching, Germany — ⁴Toray Research Center, Inc., Otsu, Japan — ⁵ilipps-Universität Marburg, Marburg, Germany — ⁶Graz University of Technology, Graz, Austria

Solid-state materials with extremely high ionic diffusion are necessary to many technologies including all-solid-state Li-ion batteries. Despite the efforts made towards the identification of crystal structures leading high lithium diffusion, only a handful crystalline structure families have been reported as Li superionic conductors.

In this work, we demonstrate that $\text{LiTi}_2(\text{PS}_4)_3$, or LTPS, shows exceptional Li-ion diffusion about an order of magnitude higher than current state-of-the-art superionic conductors. By means of extensive theoretical studies through *ab initio* molecular dynamics (backed up by several experimental characterization), we also rationalize the exceptional performances of this new superionic conductor through the concept of frustrated energy landscape.

Our work sheds light on a new family of superionic conductors and also offers a new design principle for discovering new ones.

MM 10.3 Mon 16:15 H 0106

Modeling Li_3OCl glass-electrolytes for all-solid-state Li ion batteries — •HENDRIK H. HEENEN¹, JOHANNES VOSS², CHRISTOPH SCHEURER¹, ALAN C. LUNTZ², and KARSTEN REUTER¹ — ¹Technische Universität München, Germany — ²SLAC National Accelerator Laboratory, USA

All-solid-state Li ion batteries are facilitated by using glass superionic electrolytes that combine very high Li ion conductivity and mechanical ductility. One material that has attracted much excitement is the recently reported glass-amorphous Li_3OCl . Already a superionic conductor in its crystalline form, a glass transition increases its room temperature conductivity by an order of magnitude to an outstanding 25 mS cm^{-1} [1]. The elevated mobility likely originates from a lowered

density of the liquid-like glass structure for which the ion transport mechanism has however not yet been elucidated. Based on a classical force-field [2] we explore Li_3OCl glass structures in simulation cells large enough to account adequately for long-range disorder. Via systematic melt-quench procedures qualitatively different glass ensembles are created allowing for structural heterogeneity. We use molecular dynamics simulations to analyze the ion mobility with emphasis on clarifying the influence of the structural relaxation associated with the glass transition.

[1] M.H. Braga, *et al.*, J. Mater. Chem. A **2**, 5470 (2014)[2] R. Mouta, *et al.*, Chem. Mater. **26**, 7137 (2014)

MM 10.4 Mon 16:30 H 0106

Understanding Cation-Disordered Cathode Materials — •ALEXANDER URBAN — University of St Andrews, Scotland, UK — University of California, Berkeley, USA

Cation-disordered transition-metal (TM) oxides have recently emerged as a new class of high-energy-density cathode materials for Li-ion batteries [1]. We previously showed that the practical capacity of disordered cathodes can be well estimated using percolation theory [2] and that high-throughput (HT) first principles calculations can be used to screen for novel materials in well-defined composition spaces [3]. However, apart from HT calculations, the discovery of novel disordered materials has mostly been guided by intuition.

Here, we combine a normal-mode analysis of TM site distortions with a tight-binding model and density-functional theory calculations to identify a specific electronic-structure mechanism that affects cation disorder in TM oxides. We show that d^0 TM species (Ti^{4+} , Nb^{5+} , Mo^{6+} , etc.) promote disordering, whereas TMs with other d -band fillings, especially d^6 TMs (e.g., Co^{3+}), destabilize the disordered phase [4]. This mechanism explains the stability of the known disordered cathodes and provides a simple guideline for the design of novel disordered compositions.

[1] Lee, Urban, Li, Su, Hautier, Ceder, *Science* **343** (2014) 519–522.[2] Urban, Lee, Ceder, *Adv. Energy Mater.* **4** (2014) 1400478. [3] Urban, Matts, Abdellahi, Ceder, *Adv. Energy Mater.* **6** (2016) 1600488.[4] Urban, Abdellahi, Dacek, Artrith, Ceder, *Phys. Rev. Lett.* **119** (2017) 176402.

MM 10.5 Mon 16:45 H 0106

Interfacial challenges in solid-state Li-ion batteries: Towards multiscale simulations of working interfaces — •SIMON P. RITTMAYER¹, JOSEF GRANWEHR², CHRISTOPH SCHEURER¹, and KARSTEN REUTER¹ — ¹Theoretische Chemie, TU München — ²IEK-9, Forschungszentrum Jülich

The concept of an all-solid-state battery promises gains in safety and durability beyond the current generation of Li-ion batteries. While solid-state electrolytes with sufficient ion conductivity measured under idealized conditions have recently been introduced, a thorough microscopic understanding of the involved ion transport processes, in particular at and across the interface regions associated with grain boundaries, is still lacking. In a recent electrochemical impedance spectroscopy (EIS) and microscopy (LSM, SEM, AFM) study [1], mobilities in the highly conductive LATP battery material could be correlated with bulk and interfacial structural motifs. Rational material improvement based on explicit ion dynamics simulations, however, requires detailed atomistic structures for bulk and interfaces not directly accessible from these experiments. We thus present our recent combined experimental and theoretical efforts based on a newly parametrized polarizable force field for LATP. Following the spirit of *ab initio* structure prediction, this allows us to develop an atomistic structural model of the corresponding interface regions. We further give a perspective on how to improve our sampling scheme by introducing high-resolution TEM images into an experiment-assisted score function.

[1] A. Mertens *et al.*, Solid State Ionics **309**, 180 (2017).